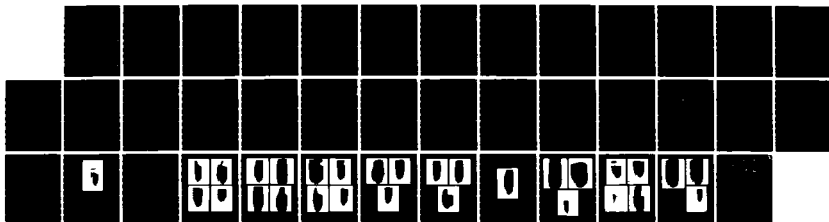


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ELECTRONIC SPECTRA OF VARIOUS LIQUIDS UNDER SHOCK CONDITIONS

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10/01/84 - 9/30/85

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A series of experiments is described in which the time resolved spectra of several liquids have been recorded as they were compressed by shock waves reverberating between two sapphire plates. The extent of chemical reaction is reported as indicated by red shift of the uppermost absorption band in the UV or visible. Most of the liquids were organic materials containing 0,1 or 2 carbon double bonds. Unsaturated substances are, on the whole, more reactive than saturated ones, but the relation is not simple. One of		

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The few inorganics studied was HI, which reacted very rapidly and in two stages. Some comments on possible mechanism are included, along with cautions about the interpretation of this kind of experiment. *Keywords:*

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I. INTRODUCTION

The purposes of this research are (i) to develop spectroscopic methods for studying chemical reactions in condensed materials as they are dynamically compressed by shock waves, and (ii) to apply these methods to the study of interesting materials. The methods developed involve absorption and reflection spectroscopy in the visible and near UV for samples which ring up to an arbitrarily chosen pressure by a succession of shock waves. Details of the experiments have been described in previous annual reports and in Ref. ¹⁻²; * the scheme of the experiments is indicated in Figs. 1-4.

Figure 1 shows the layout of the 50 foot long gas gun which accelerates a one kilogram projectile to the velocity necessary to produce the desired pressure. The breech containing high pressure gas is at the left. The target chamber is at the right, and the sample is mounted in a target holder at the end of the barrel. The projectile and target are shown in the sketches of Fig. 2. The four-inch diameter projectile has, mounted on its face, a slotted aluminum cylinder which supports a one-inch diameter sapphire impactor. At the base of the cylinder, and inside it, is a front-surfaced mirror mounted at an angle of 45° to the projectile axis. At the moment of impact of the cylinder and target the Xe flash lamp mounted in the target is directly opposite the slotted cylinder. Light from the lamp falls on the 45° mirror and is directed through the impactor, through the cell contained in the target, and hence to a spectrograph and streak camera. The cell consists of a thin layer of liquid encased in a cylindrical brass shell and bounded front and back by sapphire disks, as shown on the right side of the figure. The target holder is adjusted before the experiment so that the tilt between the plane faces of impactor and cell is less than 0.5 milliradians.

The impact between impactor and the front face of the cell produces shock waves which run forward into the front cell piece and backward into the impactor. The forward-running wave

* References are listed at the end of Section V.

induces a shock wave of pressure less than the impact pressure when it reaches the liquid sample. There follows a series of reverberations in the liquid layer between front and back sapphire disks. These eventually bring the pressure in the sample up to the impact value. The pressure buildup in a 100 micron thick sample of carbon disulfide is shown in Fig. 3. It is calculated from the shock wave jump conditions, an elastic equation of state for sapphire, and an equation of state for carbon disulfide developed by S.A. Sheffield.³ The accuracy of this calculation has been confirmed this year in a series of experiments described in reference 4. Experiments in this configuration are limited to less than approximately 130 kbars because sapphire begins to lose transparency at that pressure.

Most of the work done during the course of this contract has been on liquid CS₂. The past year has been devoted principally to exploration on other liquids, and these are best understood with CS₂ results as reference.

The absorption spectrum of a 160 micron layer of CS₂ obtained with a spectrometer is shown in Fig. 4a. The position of the 3500 Å absorption edge shown in the figure varies with pressure and temperature. In the experiments reported here the spectrum of CS₂ as it is shocked is recorded on film by means of spectrograph and streak camera, and variations of the band edge are correlated with time, pressure and temperature. The records consist of photographic films in which film density varies with wave length and time while pressure changes. A copy of one of the records is shown in Fig. 4b. Time in this figure increases vertically upward and wavelength increases horizontally from right to left. The band edge of interest is shown on the right at approximately 3600 Å before the shock reaches the sample. The flash lamp is turned on at the bottom of the figure, and its intensity builds up during time before impact. Impact occurs at time zero on the figure, and approximately 280 nsec later the shock wave enters the CS₂ sample. When it does so, the band edge takes a step to the left by an amount approximately proportional to the pressure. As pressure in the cell rings up to its final value (as in Fig. 3), the band edge steps to the left at each shock reflection. Pressure has nearly reached its final value when the

band edge is at 5500 \AA , indicated by the dark vertical line through the figure. Pressure remains constant during the next 250 nsec while the band edge shifts farther then returns to a more or less constant value. At the end of this period a reflected rarefaction from the back face of the cell reaches the CS_2 and produces a rapid decrease in pressure. This is accompanied by a reversal of the band edge shift. Pressure rings down, but has not yet returned to zero when the experiment is terminated by fracture of flash lamp or sapphire.

By comparing calculated curves of pressure vs. time, as in Fig. 3, with measured values of band edge position from records like that of Fig. 4b, it is possible to construct the curve shown in Fig. 5. The ordinate in this figure represents the shift of wave length in Angstroms produced by a given pressure, plotted as abscissa in the figure. The points shown are measured and represent five different experiments with different impact pressures and different sample thicknesses. This type of loading will be denoted "SWL" or "Step Wise Loading". It refers to "thick cell" experiments, thickness being in the range 100 to 300 microns. The curve shown represents a least squares fit to the points:

$$\Delta\lambda(\text{\AA}) = 26.79p - 0.2588p^2 + 0.00216p^3 \quad (1)$$

with p in kilobars. It represents the measurements quite well, as can be seen from the figure. Some of the differences between measured and fitted values may be due to variations in impact pressure. Equation (1) should not be used for p greater than 89 kilobars because the nature of the reaction process changes at that pressure.

II. SUMMARY OF OBSERVATIONS IN CS₂

A. Reversible and Irreversible Reactions

When impact pressure is less than 89 kilobars, the reaction represented by band edge shift appears to be completely reversible. This is suggested by Fig. 4b and confirmed in other experiments in which pressure falls to zero before the experiment is terminated. There is a residual displacement of the band edge at zero pressure, but it appears to have a magnitude to be expected from residual temperature which exists because of the dissipative character of shock compression. When impact pressure exceeds 89 kilobars, the band edge continues to shift toward the red after pressure has become essentially constant. The rate of shift increases monotonically with overpressure above 89 kilobars, and the band edge eventually goes off scale at about 7000 Å. If pressure is released before the band edge goes off scale, the edge returns toward the blue. Its final position lies above 3500 Å by an amount which appears to be a measure of progress of the irreversible reaction.

These remarks apply to the time scale of these experiments. The results of static measurements performed by Agnew and Swanson at Los Alamos show that the static threshold for irreversible reaction is considerably lower than that which we report.⁵ This implies that reaction in our experiments is proceeding from a metastable state, and that reaction paths may, therefore, differ from those recorded in quasi-static experiments.

B. Pressure and Temperature Effects

By heating or cooling the sample before it is shocked it is possible to vary the $\Delta\lambda$ vs P curve shown in Fig. 5. From such measurements it is possible to separate the effects of pressure and temperature. The results of these experiments can be accurately expressed by the following relation among band edge position (λ), pressure (P), and temperature (T):

$$\lambda(\text{\AA}) = \sum_{n=0}^3 \sum_{m=0}^2 A_{nm} P^n X^m \quad (2)$$

where $X = T (^{\circ}K) - 295$

$$A_{nm} = \begin{pmatrix} 3550 & .379 & 7.47 \times 10^{-4} \\ 12.15 & .0492 & -4.38 \times 10^{-6} \\ -.132 & -5.11 \times 10^{-4} & 5.58 \times 10^{-7} \\ 1.69 \times 10^{-9} & 0 & 0 \end{pmatrix}$$

and P is in kilobars.

The range of validity of this expression is:

$$\begin{aligned} 0 &\leq P \leq 50 \text{ kb} \\ 200 &\leq T \leq 700 ^{\circ}K \end{aligned}$$

Within this range it represents measurements with an error less than 1%. This equation also encompasses the static measurements at room temperature reported by Agnew and Swanson (op cit.).

C. Dilution

When diluted in hexane or ethanol, the band edge shift is well represented at 50 kbars, for moderate dilution, by the straight line

$$\Delta\lambda(\text{\AA}) = 200 + 800x$$

where x is volume fraction of CS_2 , $x > 0.1$. When the CS_2 fraction is less than 10%, the curve turns downward rapidly and $\Delta\lambda$ appears to vanish at infinite dilution.

D. Reflection

Reflected spectra show that CS_2 under the loading described here behaves like a poorly conducting metal at wavelengths shorter than that of the band edge. At longer wavelengths it is transparent, at least in the region of reversible reaction.

E. Conclusions

Band edge shift in the UV and visible is a "good" parameter for monitoring reactions, applying equally well to single shock, multiple shock, and isentropic experiments in liquids.

The observed reactions are multimolecular and do not occur at infinite dilution.

The extensive observations on CS_2 are commensurate with a process wherein rapid compression produces, reversibly, platelets of an electrically conducting substance which are a few microns in diameter and a few tenths of a micron thick.

There are at least three identifiable reaction stages in CS_2 : the reversible stage described above, a second reversible stage in the pressure range 89-91 kilobars which absorbs weakly at wavelengths longer than 5500 Angstroms; and a third stage which is irreversible and which progresses at a rate which increases rapidly with pressure at pressures above the 89 kilobar critical pressure.

III. OBSERVATIONS ON OTHER LIQUIDS

The principal reasons for diversion of research effort from CS_2 to other liquids during this past year have been to determine whether or not the spectral changes observed in CS_2 are unique to that material and to provide some guidance to other compounds which may also undergo major changes as a result of stepwise shock loading. A secondary objective has been to attempt to choose materials whose response to SWL may provide some clue to the microscopic chemical processes which are occurring during SWL. Compounds examined have been almost exclusively organic. Stable and metastable compounds have been included. Materials and results are summarized in Table I.

It has been suggested by Yakusheva, Yakushev and Dremin⁶ that shock-induced chemical reactions occur more readily in unsaturated than in saturated carbon compounds, and that the

reaction is pyrolysis, with free carbon and saturated carbon compounds as products. More recently M. Nicol⁷ has proposed that the process is not pyrolysis, but polymerization. He supports this suggestion by pointing to the observed polymerization of benzene under static pressures of the order of 100 kilobars.

It was largely because of the earlier Russian work, Nicol's suggestion, and the fact that CS₂ itself contains 2 double carbon bonds that the strong emphasis displayed in Table I was placed on carbon compounds. Materials are grouped according to the number of carbon double bonds, and some experiments were done on benzene and benzene derivatives.

Inorganic materials were limited to CS₂, water and HI.

In the copies of spectrograms shown in Figs. 6-14, time runs from left to right and wavelength increases upward.

The entries in Table I are, column by column:

1. The number of the figure which contains a copy of the time resolved spectrogram.
2. Shot number.
3. Sample material.
4. Sample thickness in microns.
5. Impact pressure in kilobars.
6. Statement of pressure reversal. This is achieved by using a thin sapphire back piece to the cell and allowing the rarefaction from its free surface to return to quench the sample.
7. The expected red edge of the uppermost absorption band in the UV and visible under ambient conditions. This is taken from spectral tables as the wavelength at which transmission is reduced 20% for the most concentrated sample. No entry implies that values were not readily available.

8. This is the apparent band edge before impact shown in the spectrograms. When $\lambda_o \gg \lambda_n$, the apparent cut off is probably due to the optical system.
9. $\Delta\lambda$ is the amount by which band edge is shifted toward the red from λ_o when pressure has rung up to 95% of the impact value. When \geq appears before the number, it implies that the number is the recorded shift, but the preshock absorption edge was off scale in the UV.
10. $(\Delta\lambda/\Delta t)_p$: Here $\Delta\lambda$ is the shift toward the red which occurs *after* impact pressure is reached by ring up. Δt is the time it takes for this shift to occur. Their ratio is assumed to be a measure of the irreversible reaction rate in most cases.

A. Organic Materials With No Double Bonds

These are arranged in two subcategories. The first comprises four shots with nitromethane to which ethyldiamine (EDA) has been added. Earlier experiments with pure nitromethane showed small band edge shifts, but no indication of irreversible reaction, even at 130 kilobars with initial temperature increased to 125°C. Addition of EDA changes the situation dramatically, as can be seen from the table and in Fig. 6. Even at 65 kilobars there is a substantial reaction rate after calculated pressure has reached its terminal value. i.e. $(\Delta\lambda/\Delta t)_p \approx 1.1 \text{ Å/nsec}$, as shown in the last column of the Table.

The second experiment, 85-026, was constructed so that pressure release occurred after calculated pressure was constant. Here there is an increased reaction rate (2.6 Å/nsec), and a partial reversal of the shift when pressure is relieved. When this is compared with shot 85-022 (Fig. 8) in which complete reversal of the band edge in styrene is seen, it is apparent that at least part of the nitromethane has reacted irreversibly. The appearance of a new absorption band in the visible at the time when maximum band edge displacement occurs tends to confirm this. This new absorption band is in a wave length region near that expected for NO_2 , but displaced somewhat. Note that it is shifted downward toward the blue as pressure is released.

Shots no. 85-004 and 85-002 in this set show complete reaction at increasing rates as impact pressure increases. At 133 kilobars the reaction rate is greater than can be resolved with this system.

The next subcategory in A, Fig. 7, contains two solvents, CCl_4 and ethanol, for which no shift is recorded, acetone, and ethyl iodide. The shift for acetone is negligible; that for ethyl iodide is appreciable and suggests that irreversible reaction might be initiated at moderately high pressures.

B. Organics With One Double Bond

The first five experiments are with styrene arranged according to pressure. Records of the first four are shown in Fig. 8. The first two are pressure reversal shots. At 58 kilobars the residual displacement after pressure reversal is so small that one concludes that a) there has been no irreversible reaction, and b) the temperature coefficient of band edge displacement is practically nil. The first point is interesting because the record shows that edge shift continues after pressure has rung up, suggesting that we are seeing a two stage reaction, both reversible. This same effect is seen in all of the styrene shots, and the rate increases as pressure increases, except for 85-014. The last appears to be anomalous and the pressure region above 100 kilobars should be investigated further.

Shot no. 85-021 is similar to 85-022, but pressure is greater and band edge does not return to near zero on pressure reversal. This is attributed to a partial irreversible reaction. Shot no. 85-017 also had a pressure reversal. Its record is faint, but it suggests that some recovery of the band edge may have occurred. Shot no. 85-014 is not shown in the figures. The record is similar to 85-017 with smaller $(\Delta\lambda/\Delta t)_p$. It is conceivable that a different reaction is occurring.

Fig. 9 shows records for dichloroethylene, hexene, and acrylonitrile. The first shows a small band edge shift, and a much larger one has occurred if λ_n is far below the detection limits of the system. It is to be noted, however, that there is no indication of continuing reaction in the constant pressure region. Hexene shows no shift, but its normal band edge is off the record. It is apparent, however, that no major reaction has occurred. The shock chemistry of acrylonitrile has been thoroughly studied by Yakushev, Nabatov and Yakusheva.⁸ Using color film in a streak camera, they noted increased absorption in the blue between 50 and 70 kilobars and complete loss of transparency above 70 kilobars. The record shown in Fig. 9 provides a quantitative

record of the effects they report. They suggest that pyrolysis is occurring according to the formula:



but a lengthy study would be required to confirm or negate this suggestion.

C. Organics With Two Double Bonds (Hexadiene)

The first experiment, no. 85-030 with the 1,5 isomer, shows no effect at 101 kilobars. The second, at 129 kilobars, also with 1,5, shows a peculiar momentary loss of transparency across the entire spectrum. It is reminiscent of observations on water (Fig. 14), where the possibility of a phase transition is suggested. As of this writing I place little credence in the record. It should not be ignored, neither should it be accepted without further study.

The 2,4 isomer, shot no. 85-031, is dramatically different from the 1,5. There is a large shift in the band edge, and an oscillation of the edge after ringup to 130 kilobars. This is an intriguing record and the material is a good candidate for further study. Note also that there is a loss of transparency all across the record after ring up pressure is reached. This is conceivably an artifact, and it requires further study. It is also conceivable that it may be related to the electrical oscillations in CS_2 reported by Sheffield⁹.

D. Organics with One Triple Bond

Category D contains only one member, 2-butyne with one triple carbon bond. The record is shown in Fig. 11. No spectral change is observed.

E. Benzene and Derivatives

Category E, Fig 12., shows records from two experiments with benzene and one with nitrobenzene. Shot no. 84-053 shows benzene to be reversible at 112 kilobars with no continuing reaction at constant pressure. Shot no. 84-052 at higher pressure shows a larger shift and a possible beginning of constant pressure reaction, but the record terminates anomalously, possibly due to sapphire failure. Record no. 85-003 for nitrobenzene shows a much larger shift, loss of transparency above the band edge, and no motion of the band edge at constant pressure. This record has an unexplained anomaly. The band edge before shocking is at 3955\AA instead of 2700\AA ; the test flash shows the same effect. One possibility is that the flash lamp was inadvertently made with soft glass instead of quartz. Further experimentation will be required to determine the true situation.

F. Inorganics

The first group consists of four experiments with carbon disulfide, Fig. 13. The first two, nos. 84-049 and 84-051 are pressure reversal shots with impact pressure above the irreversibility threshold of 89 kilobars. The first of these, 84-049 at 90 kilobars shows that the band edge is recovered after some irreversible reaction has taken place, but its final position is well above that which exists when no reversible reaction occurs. The second, no. 84-051 at 94 kilobars, shows that the reaction has progressed to a point where the band edge is not recovered by reversal of pressure.

Shot no. 84-050 was made in an attempt to fill in the dilution curve for small concentrations. The record is faint and the band edge shift somewhat uncertain, but the result is in reasonable accord with other measurements.

Shot no. 85-034 was a thin cell experiment done to verify the cooling effect which has been inferred from earlier experiments. It confirms the observation that compression of a very thin CS_2 sample between two sapphire plates is very nearly isothermal.

The second group of inorganics consists of two water shots and one with hydrogen iodide, Fig. 14. The two water shots were made with slightly different geometries to eliminate the possibility that the loss of transmission across the entire spectrum was due to reflection from a sapphire interface. There remains some doubt about the validity of the observed opacity because of a discrepancy between the two records. Shot no. 84-040 has the transparency gap occurring at pressures between 107 and 113 kilobars. Shot no. 84-048 gives 96 to 107 kbars. As for the hexadiene shot noted above, the effect should be noted for further study, but not accepted absolutely at this stage.

The HI shot, also shown in Fig. 14, is dramatically unexpected. The first shock, with amplitude of approximately 12 kilobars, moves the absorption edge up about 300\AA and produces some loss of transparency up to about 5000\AA , as would be expected from dissociation and absorption by iodine. The second shock, which brings the total pressure to about 35 kilobars, produces immediate and total opacity. It seems unlikely that either bubbles or particulate matter could form in this short time; but if the record represents the true state of the sample, dramatic and unexpected changes of state are surely occurring. It's interesting to note that the polymerization of a sister compound, HF, has been reported from the vapor phase.

IV. DISCUSSION

There is a certain hazard in conducting a survey of the kind described in this report. The experiments are very difficult, and it is always possible that the observed effect in a single experiment is an artifact. That point has been made several times in the above section, and the reader should take it very seriously. The only way to assure that the effects are real is to

conduct sets of experiments in which parameters are varied in such a way as to eliminate or define the artifacts carefully. Having said this, I shall also say that we now have had a great deal of experience in doing these kinds of experiments, and I think the results are reliable, with the exceptions noted in Section III.

Equations of state (EOS) remain a serious problem. Experiments have shown that pressure calculations in CS_2 are very accurate, and there is some evidence from static measurements that calculated temperatures are reasonable. All of the other liquids have been represented by Mie-Gruneisen equations of state using the Woolfolk, Cowperthwaite, Shaw "Universal Liquid Hugoniot P-V Relation."¹⁰ Specific heat is usually obtained from a parabolic approximation to the Debye function; sometimes it is taken to be constant. Because of similarities among liquids it is unlikely that calculated pressures are far off. Impact pressures depend only on sapphire properties and impact velocities, so they are well known.

For many purposes the uncertainty in equation of state is of little consequence. In other cases it is critical, as when comparing the pressures at which opacity occurred in water shots 84-040 and 84-048. Another example is in the bilinear relation between band edge wave length and pressure in nitromethane. In 85-004 the corner is at approximately 80 kilobars; in 85-028 it is at 75 kilobars. Given the present state of knowledge of EOS, one should assume these values to be the same. More experiments or a better EOS would resolve the question.

Two serious questions involve preshock band edge positions for water and nitrobenzene. Herzberg gives a value of 1900\AA for band edge in pure water.¹¹ Bohren and Huffman¹² show a sharp increase in absorption below about 2000\AA . Water used in our experiments was distilled, but it is possible that contamination occurred from interaction with cell components. If contamination exists to the extent that band edge is raised from 2000 to 3200\AA , the transparency loss, if it is real, may be related to contaminant behavior.

The value of 2700\AA for band edge of nitrobenzene was taken from the TRCHP tables.¹³ The data reported there are for a very dilute sample. Absorption tails off very slowly with increasing wave length, and we may be seeing the effect of going from a very dilute sample to the pure material.

Two styrene experiments, 85-009 and 85-017 were nearly identical in impact pressure and cell thickness. They differed in that the reaction inhibitor in 85-009 had been removed by distillation; 85-017 contained as-received material. $\Delta\lambda$ was almost the same for both, but $(\Delta\lambda/\Delta t)_p$, was three times greater for as-received than for the distilled sample. The difference is evident from cursory examination of the records. The reason for it is not evident.

In looking at the entire series of organic liquids in Table I, it is evident that the existence of unsaturated carbon does not dramatically effect shock-induced reactions in the pressure range we have covered. The difference between 1,5- and 2,4-hexadiene illustrates this well, as does the failure of 2-butyne to react. It is possible that major differences between saturated and unsaturated carbon compounds will appear at higher pressures. To achieve these will require considerable effort in development of new techniques and calibration of other materials.

Some interesting candidates for further study do appear from this survey. My choices would be variants on nitromethane, including methyl nitrite, ethyl iodide, styrene, hexadiene, nitrobenzene, water and hydrogen iodide. The last-named is particularly interesting. It is one of the few diatomics which can be readily studied, and its simplicity makes it attractive for theoretical studies.

The last column in Table I gives $(\Delta\lambda/\Delta t)$ at "constant pressure". This should be taken with a grain of salt. At least some of the observed reactions will be exothermic. To the extent that they are, pressure will increase as heat is released, so pressure may, in fact, be varying a great deal during this phase of the reaction process. Mechanical measurements to determine such effects would be interesting and entirely feasible.

V. ACKNOWLEDGEMENTS

Experiments described here were carried out by Joel Hegland, Richard Granholm, and Jeff Furrer, with advice and counsel from Paul Bellamy. They have done an excellent job with very difficult experiments, and I wish them to know that their conscientious efforts have been deeply appreciated.

1. G.E. Duvall, K.M. Ogilvie, R. Wilson, P.M. Bellamy, and P.S.P. Wei, "Optical spectroscopy in a shocked liquid," *Nature*, 296, 946 (1982).
2. K.M. Ogilvie, G.E. Duvall, "Shock-induced changes in the electronic spectra of liquid CS₂," *J. Chem. Phys.* 78, 1007 (1983).
3. S.A. Sheffield and G.E. Duvall, "Response of liquid carbon disulfide to shock compression: Equation of state at normal and high densities," *J. Chem. Phys.* 79, 1981 (1983).
4. G.T. Sutherland, "Pressure profile of multiply-shocked carbon disulfide", *J. Appl. Phys.*, 59, 1141 (1986).
5. S.F. Agnew and B.I. Swanson, "Spectroscopic studies of carbon disulfide at high pressure", APS Topical Conference, Shock Waves in Condensed Matter, Spokane, WA, July 22-25, 1985, Plenum Press (to be published).
6. O.B. Yakusheva, V.V. Yakushev, and A.N. Dremin, "Relation between loss of transparency by carbon compounds under high dynamic pressures and 'anomalies' on the impact compressibility curves," *Russian J. Phys. Chem.* 51, 973 (1977).
7. M. Nicol, Chem. Dept., UCLA. Private communication.
8. V.V. Yakushev, S.S. Nabatov, and O.B. Yakusheva, "Physical properties and conversion of acrylonitrile at high dynamic pressures," *Combustion, Explosion, and Shock Waves* 10, no. 4, pp. 509-518 (1974).
9. S.A. Sheffield, "Shock-induced reaction in carbon disulfide," dissertation presented in partial fulfillment of the requirement for the degree of Doctor of Philosophy, Department of Physics, Washington State University, 1978.
10. R.W. Woolfolk, M. Cowperthwaite, and R. Shaw, "Universal liquid Hugoniot P-V relation," *Thermochemica Acta* 409 (1973).
11. G. Herzberg, "Electronic spectra of individual molecules and their interpretation," *In Molecular spectra and molecular structure: Electronic spectra of polyatomic molecules*, pp. 489, Van Nostrand Reinhold Company, New York, 1966.
12. C.F. Bohren and D.R. Huffman, *Absorption and scattering of light by small particles*, John Wiley and Sons, New York, 1983.
13. Thermodynamics Research Center Hydrocarbon Project, Texas A&M University, College Station, TX 77843, "Selected UV spectral data," supplementary vol. no. C-47, 10/31/80, serial no. 105.

SHOT SUMMARY 10/1/84 - 9/30/85

I. Organic Molecules

Fig.	Shot No.	Liquid	Cell Thickness (microns)	Pressure (kilobars)	Pressure Reversal	$\lambda_n, \text{\AA}$	$\lambda_o, \text{\AA}$	$\Delta\lambda, \text{\AA}$	$(\Delta\lambda/\Delta t)_p$ $\text{\AA}/\text{nsec}$
A. No Carbon Double Bonds									
6	85-007	NM/5wt% EDA	310	65	No	3300	3354	850	1.1
6	85-026	" "	122	86	Yes	3300	3264	810	2.6
6	85-004	NM/10wt% EDA	160	100	No	3300	2900	>3100	>100
6	85-002	" "	30	133	No	3300	2900	>3200	>100
7	85-016	ethanol	110	116	No	2450	2670	<220	...
7	85-008	carbon tet	112	111	No	2750	2700	0	0
7	85-006	acetone	109	111	No	3100	3030	70	0
7	85-023	ethyl iodide	158	101	No	-	3170	540	0
B. 1 Carbon Double Bond									
8	85-022	Styrene	89	58	Yes	2950	3000	335	0.25 ^h
8	85-021	" "	94	79	Yes	"	3010	450	0.41 ⁱ
8	85-009	" " (p)	109	110	No	"	2980	900	0.55
8	85-017	" "	107	111	Yes ^a	"	3040	920	1.7
-	85-014	" "	107	123	No	2950	3025	1125	0.7
9	85-028	cis 1,2 - dichloroethylene	156	101	No	-	2690	≥ 255	0
9	85-024	1 - hexene	158	101	No	2100	2875	<775	-
9	85-010	acrylonitrile	104	110	No	-	2940	m	>100
C. 2 Carbon Double Bonds									
10	85-030	1,5 - hexadiene	155	101	No	2350	2880	<530	-
10	85-041	" "	157.5	129	No	"	2970	$\geq 710^j$	-
10	85-031	2,4 - hexadiene	160	130	No	2800	2775	670	n
D. Triple Carbon Bonds									
11	85-027	2 - butyne	155	101	No	-	3260	k	-
E. Benzene Derivatives									
12	84-053	benzene	117	112	Yes ^b	2650	2695	411	0
12	84-052	" "	305	123	No	"	2693	525	- ^f
12	85-003	nitro benzene	112	135	No	2700	3955	≥ 870	0
		vinyl benzene (styrene)				see (B) above			

SHOT SUMMARY 10/1/84 - 9/30/85

II. Inorganic Molecules

Fig.	Shot No.	Liquid	Cell Thickness (microns)	Pressure (kilobars)	Pressure Reversal	$\lambda_n, \text{\AA}$	$\lambda_o, \text{\AA}$	$\Delta\lambda, \text{\AA}$	$(\Delta\lambda/\Delta t)_p$ $\text{\AA}/\text{nsec}$
13	84-049	Carbon disulfide	21	90	Yes	3500	3450 ^d	1900	3.6
13	84-051	" "	26	94	Yes ^m	3500	3440	1800	13
13	84-050	5 vol % CS ₂ in Hexane	307	77	No	3500	3355	425 ^e	-
13	85-034	CS ₂ thin cell	0.8	55	No	3500	-3205	-1250	- ^f
14	84-040	Water	306	125	No	1900	3260 ^b	- ^c	0
14	84-048	" "	310	123	No	"	"	"	"
14	85-033	Hydrogen iodide	161	120	No	3600	3475	315-1600	see text

- a. Early light loss, but band edge reversal is indicated.
- b. Cutoff at this wavelength is apparently due to impurities.
- c. Total extinction between about 90 and 110 kbars.
- d. Impact pressure was above the threshold value and pressure reversal produces partial reversal of the band edge shift.
- e. Very faint record. $\Delta\lambda$ is uncertain.
- f. Abnormal termination of record - probably due to faulty sapphire.
- g. Band edge at 2809 \AA after pressure reverted to zero.
- h. Band edge is displaced upward approximately 13 \AA after pressure returned to zero.
- i. Band edge is displaced upward approximately 240 \AA after pressure returned to zero.
- j. Odd record, see text and Figure 10.
- k. No change observed.
- l. Heat conduction to sapphire causes band edge to move down to $\sim 3770 \text{\AA}$ within 30 $\mu\text{seconds}$.
- m. Immediate reaction produced total opacity.
- n. Band edge position oscillated after impact pressure was reached.
- p. Inhibitor was removed by distillation.

A Note on the Figures:

The time scales on Figs. 6-14 are all approximately the same: 1 microsecond is approximately equal to 1.75 times the sprocket hole period on the vertical side of each photo. Most of the records were made with a 150 line/mm grating, and for those records the spectral range is very close to 4090 Angstroms in each case. Shots No. 85-022 and 85-031 were made with a 300 line grating, and the spectral range between sprocket holes is approximately 2050 Å. Shot No. 84-050 was made with a 600 line grating and there are approximately 1030 Å between sprocket holes. A reference wave length can be obtained using the value of λ_0 given in the Table.

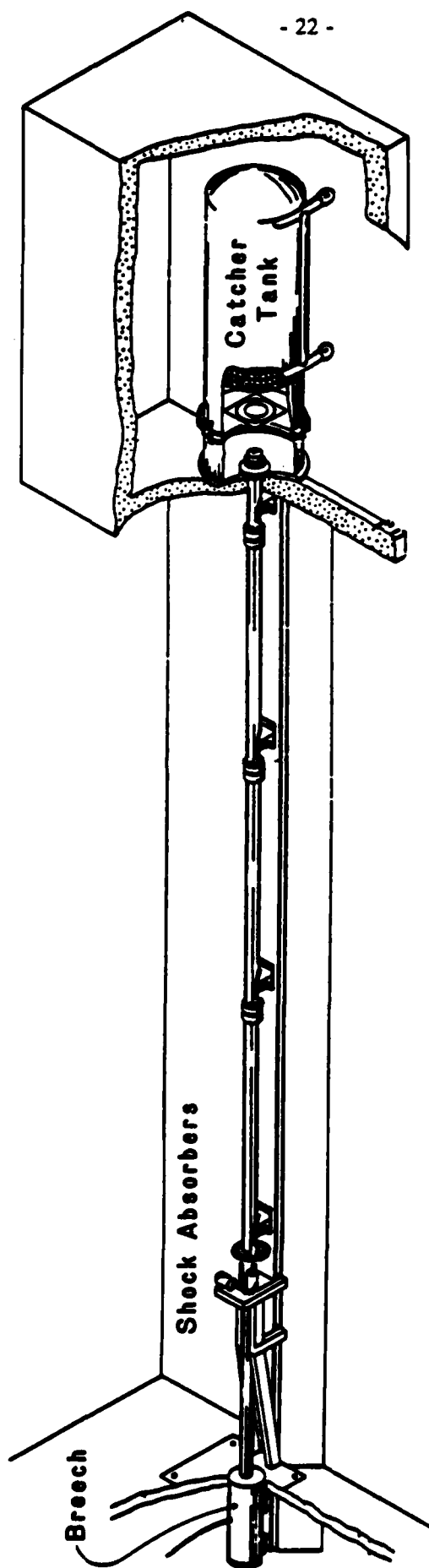


Fig. 1. Schematic diagram of single stage gas gun used to accelerate projectile. Target holder is mounted on the wall of the chamber at the right.

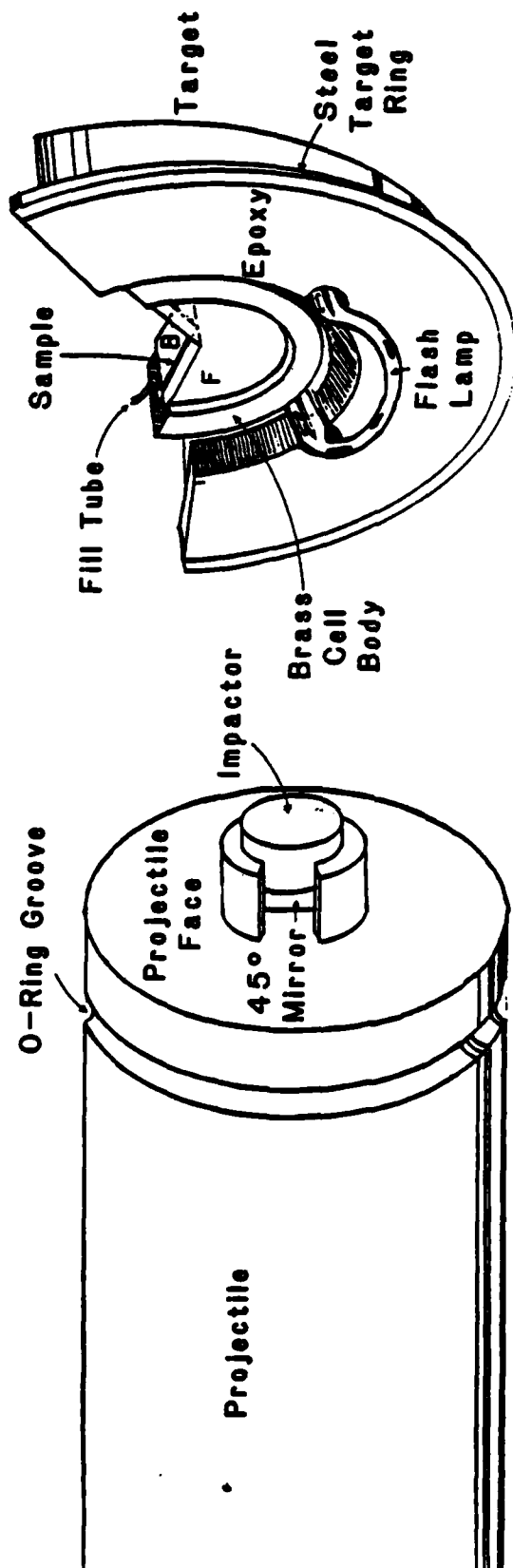


Fig. 2. Sketch of projectile face and target. Light from the flash lamp is intercepted by the 45° mirror on the projectile and turned so it passes through impactor and sample.

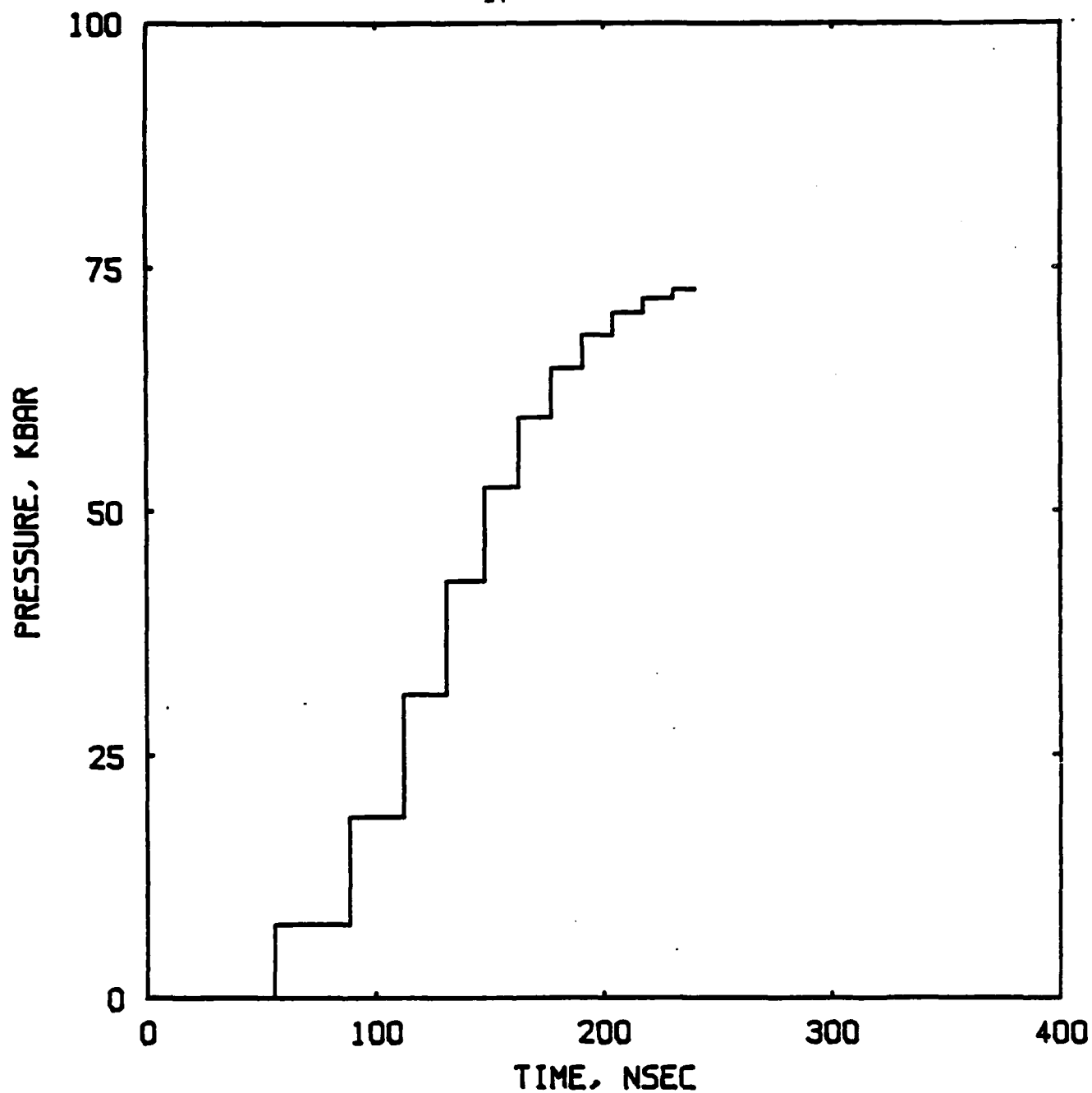


Fig. 3. Pressure in a 100 micron thick CS_2 sample between sapphire plates calculated from shock jump² conditions and the SheffieldII equation of state for CS_2 .

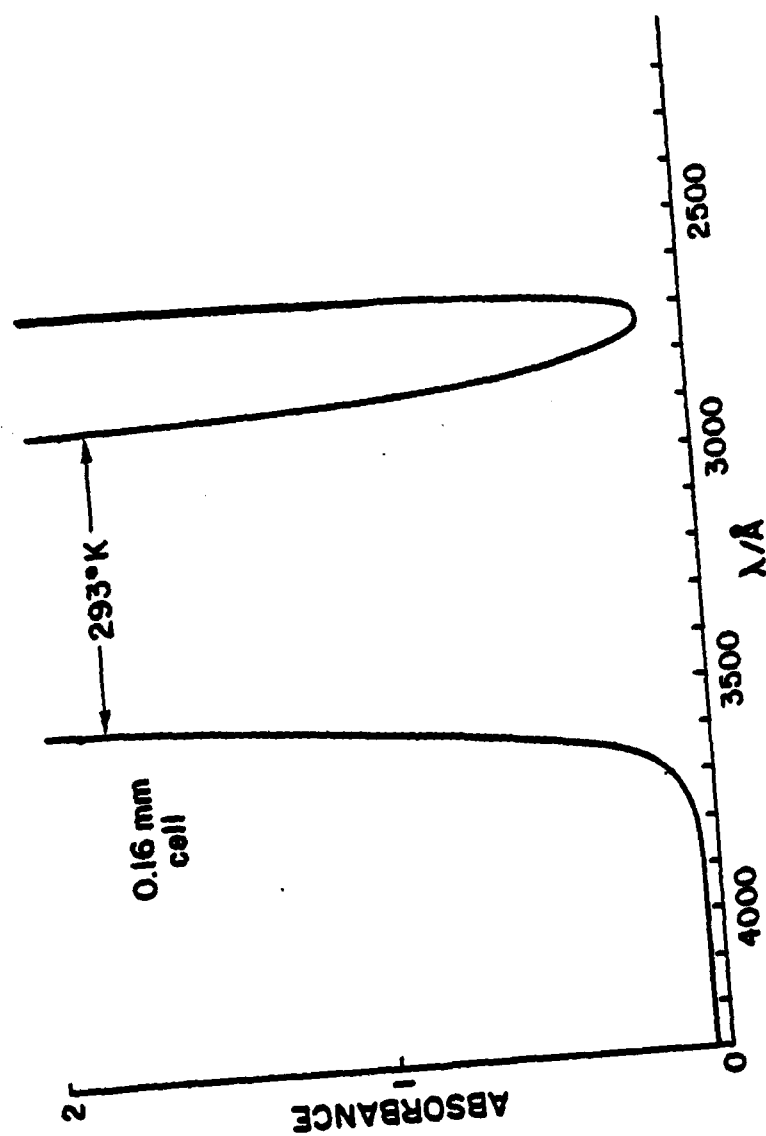


Fig. 4. a) Absorption spectrum of a 0.16 mm layer of liquid CS_2 measured in a spectrometer.

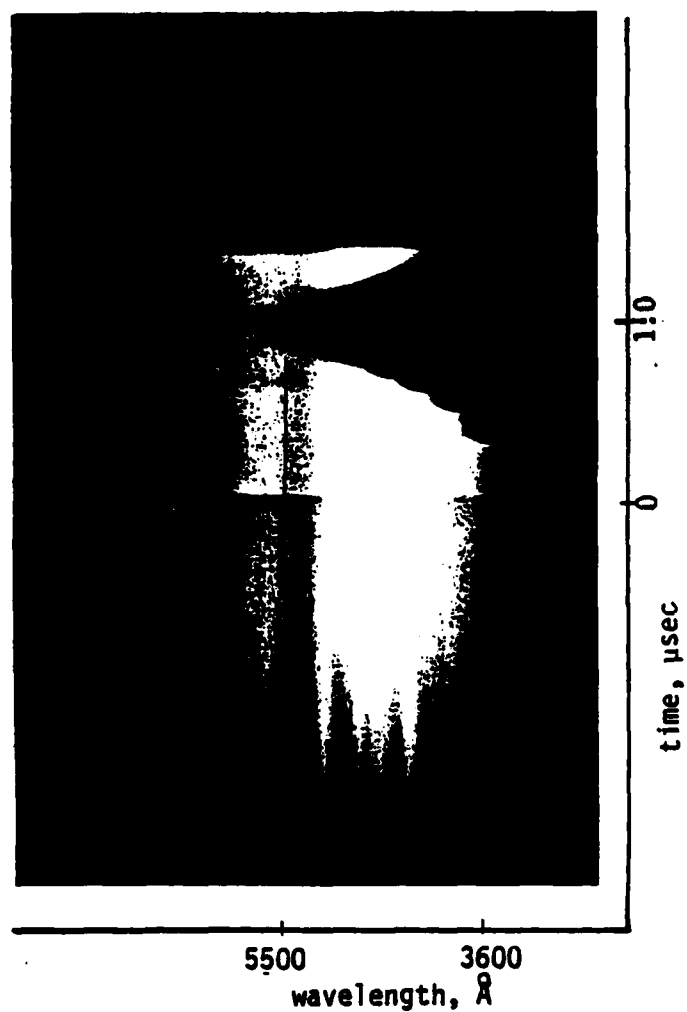


Fig. 4. b) Absorption spectrum of a 0.32 mm layer of CS₂ between two sapphire plates shocked to 77 kbar ((82-006). Time increases from bottom to top. Impact occurs at $t = 0$.

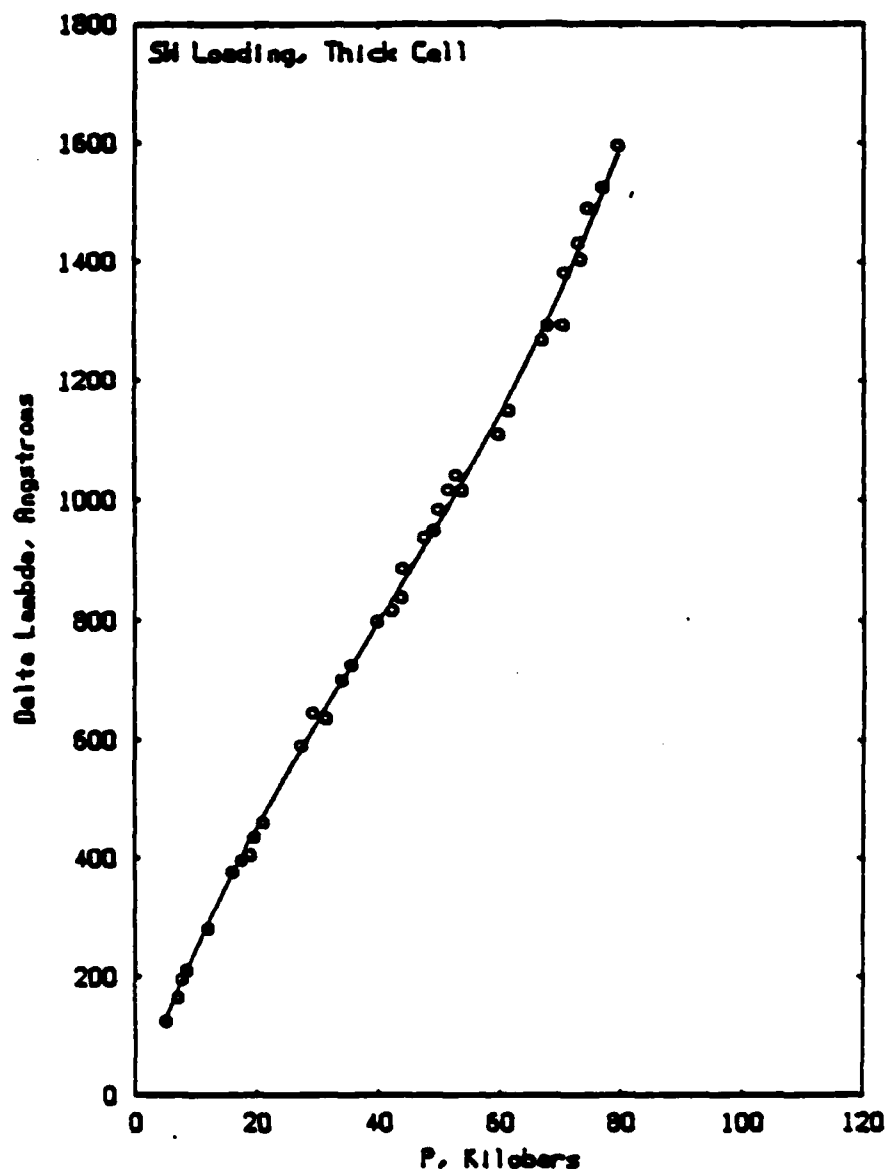


Fig. 5. Shift of red band edge due to stepwise shock loading. Reference edge is approximately 3550 Å. Points are the results of five experiments. The line is $\Delta\lambda = 26.79p - 0.2588p^2 + 0.002162p^3$, p in kbar, $\Delta\lambda$ in Å. Samples were at room temperature before they were shocked.

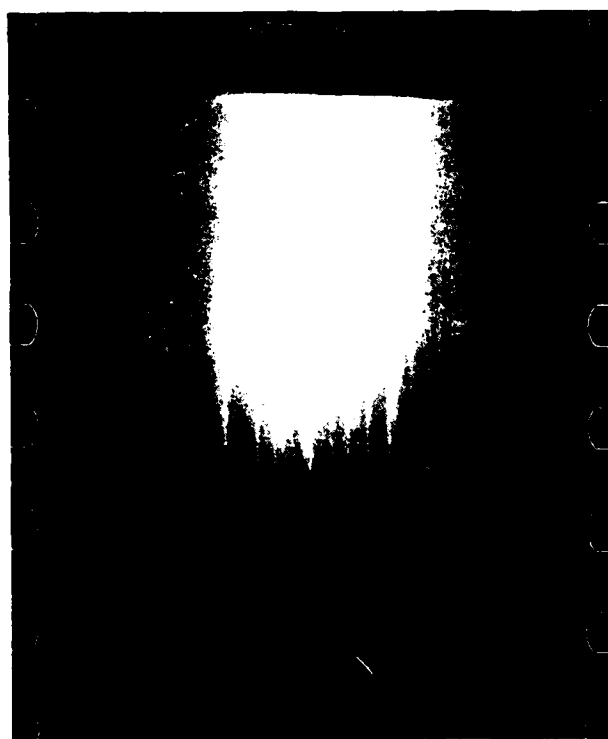
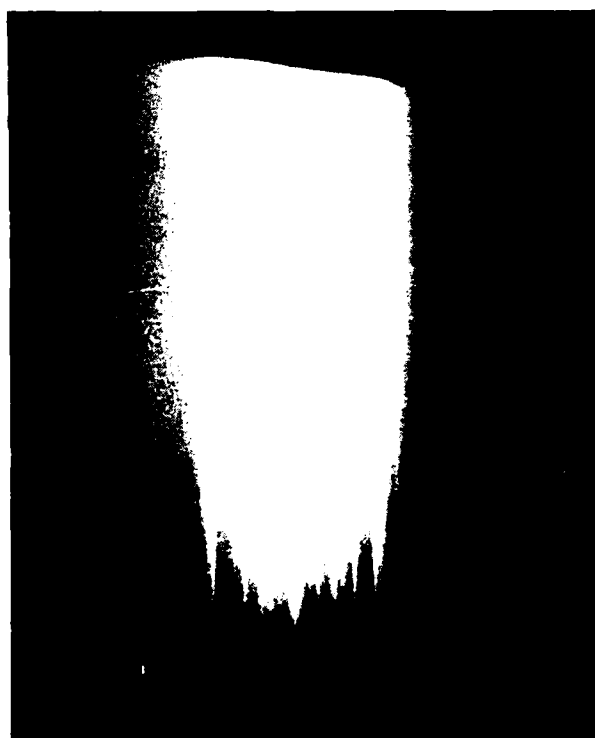
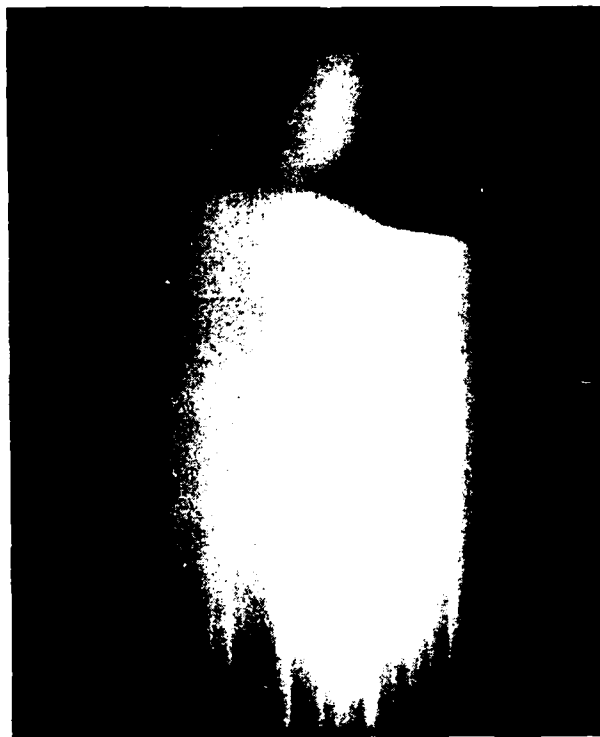
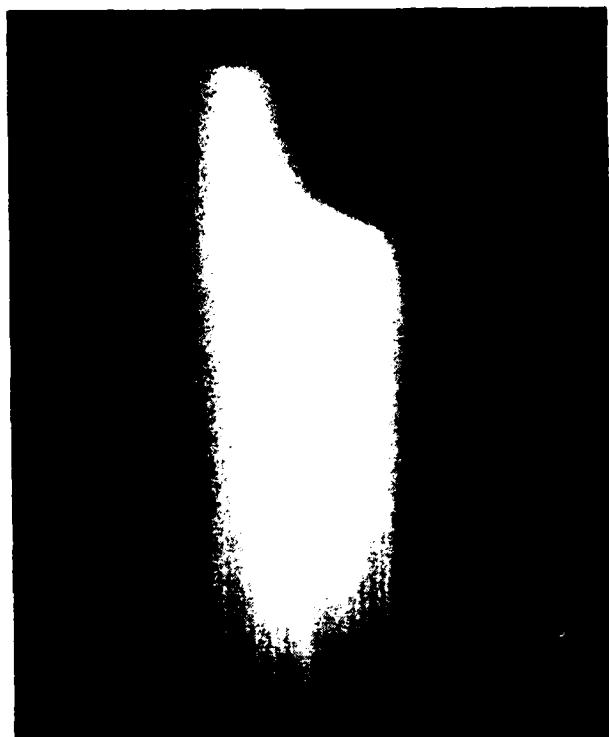


Fig. 6. a) nitromethane/5 wt% EDA (85-007)

b) nitromethane/5 wt% EDA (85-026)

c) nitromethane/10 wt% EDA (85-004)

d) nitromethane/10 wt% EDA (85-002)

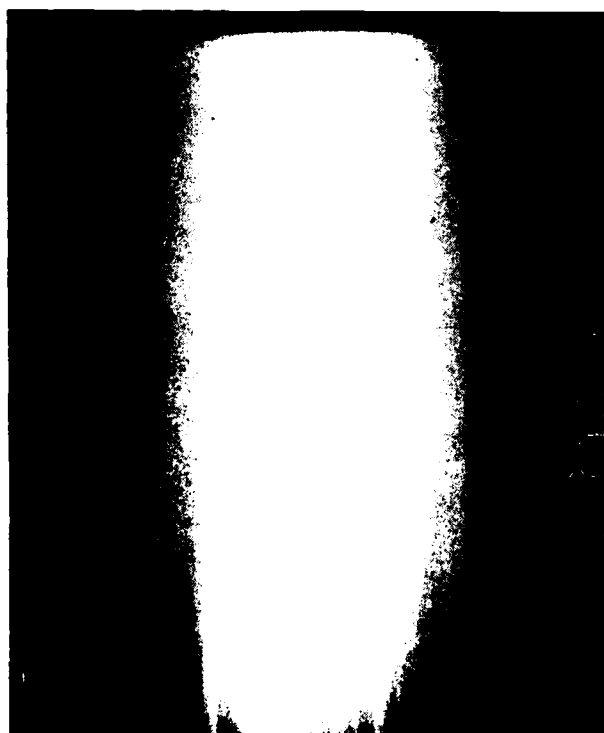
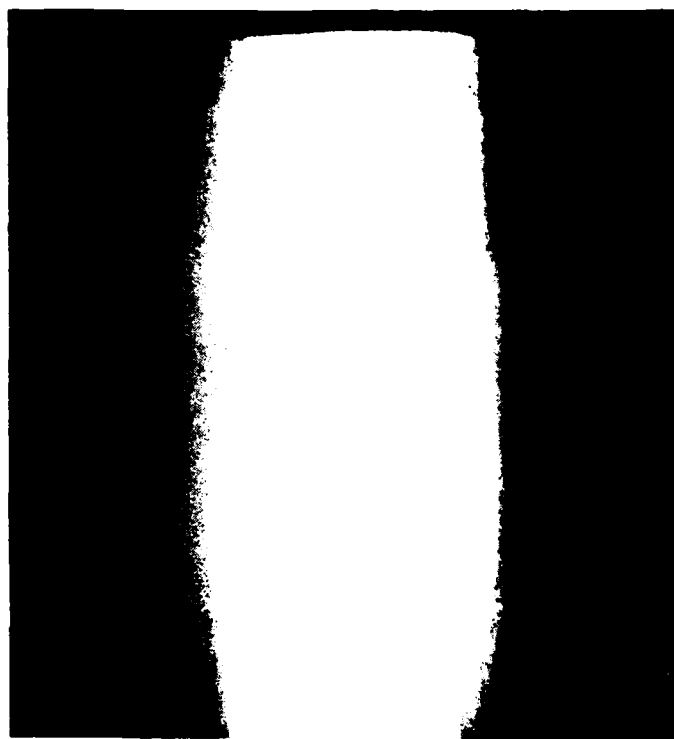


Fig. 7. a) ethanol (85-016)

b) carbon tet (85-008)

c) acetone (85-006)

d) ethyl iodide (85-023)

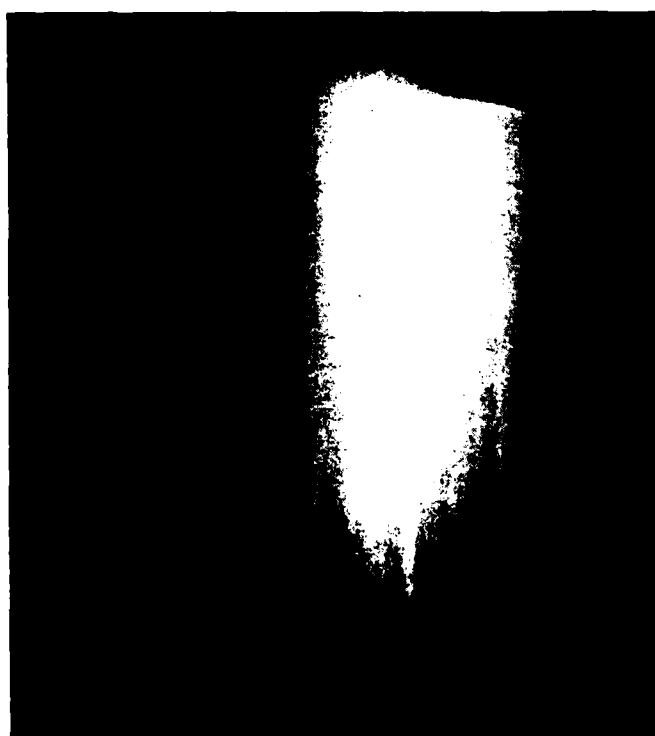
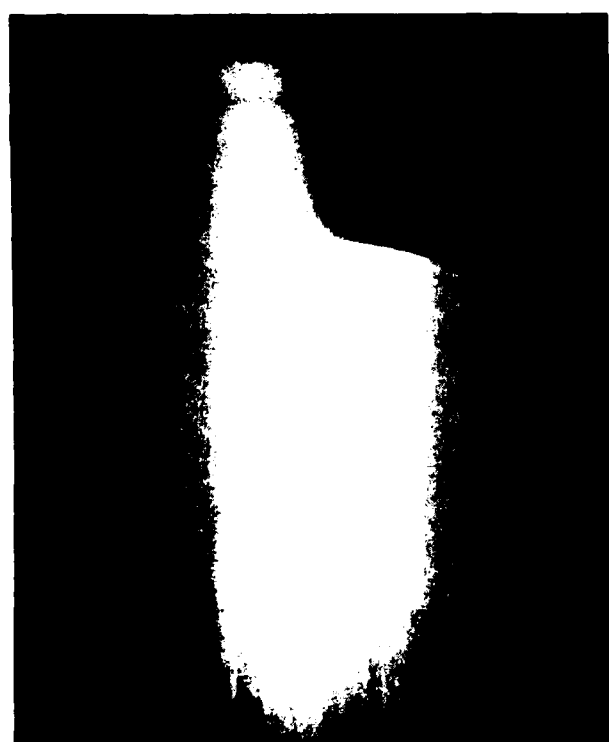
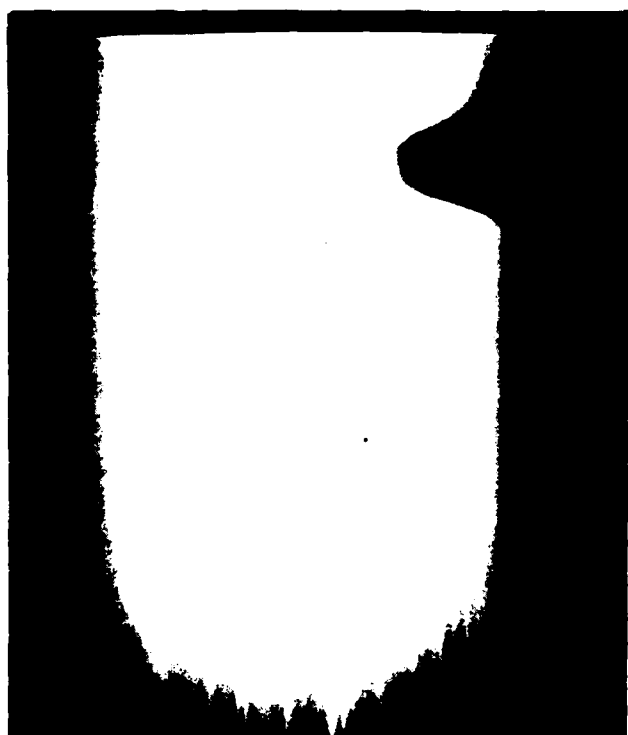


Fig. 8. a) styrene (85-022)

b) styrene (85-021)

c) styrene (85-009)

d) styrene (85-017)

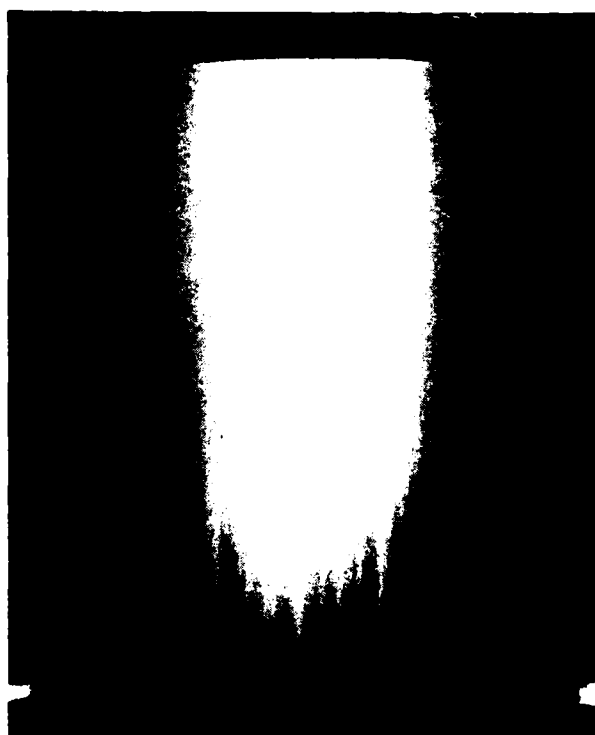
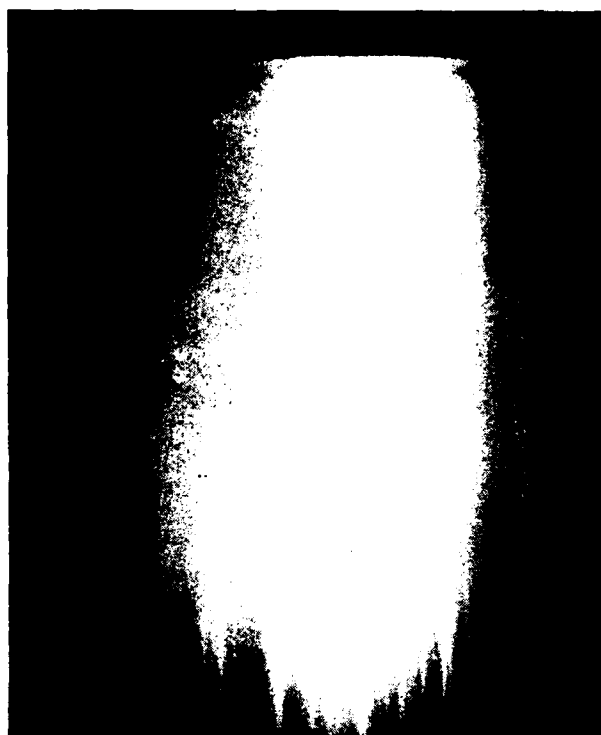


Fig. 9. a) cis 1,2-dichlorethylene (85-028)

b) 1-hexene (85-024)

c) acrylonitrile (85-010)

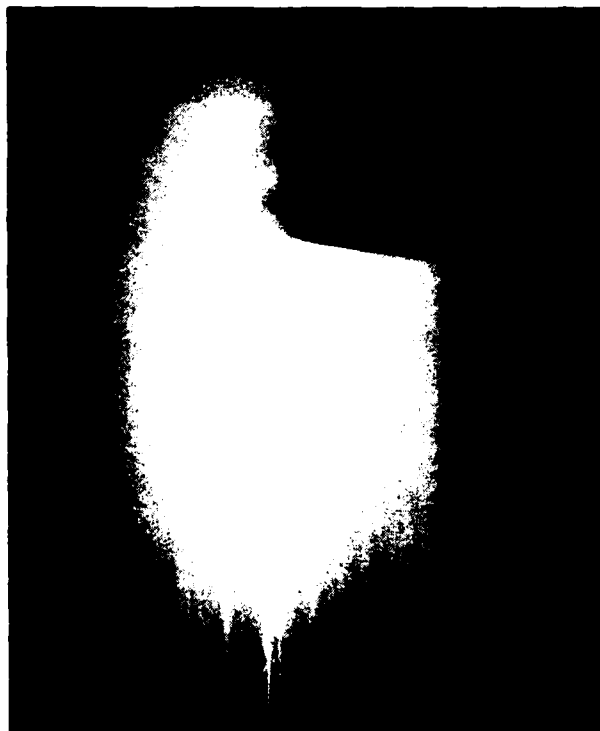
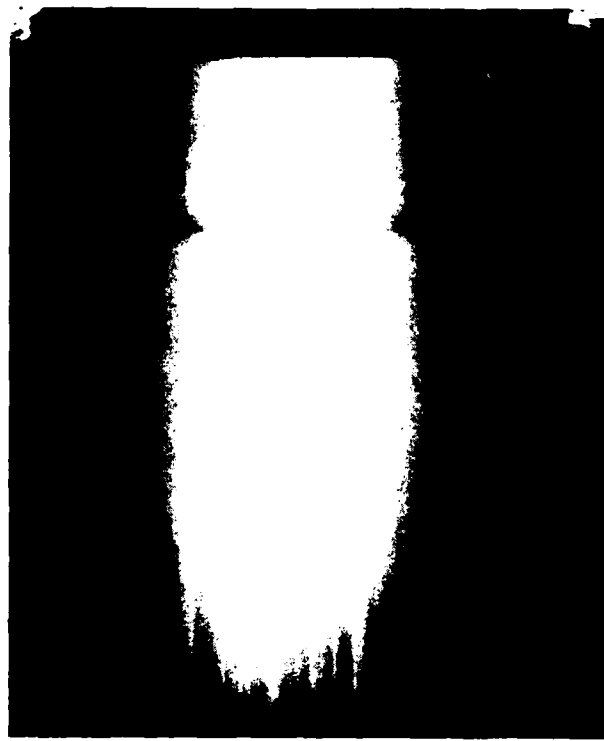
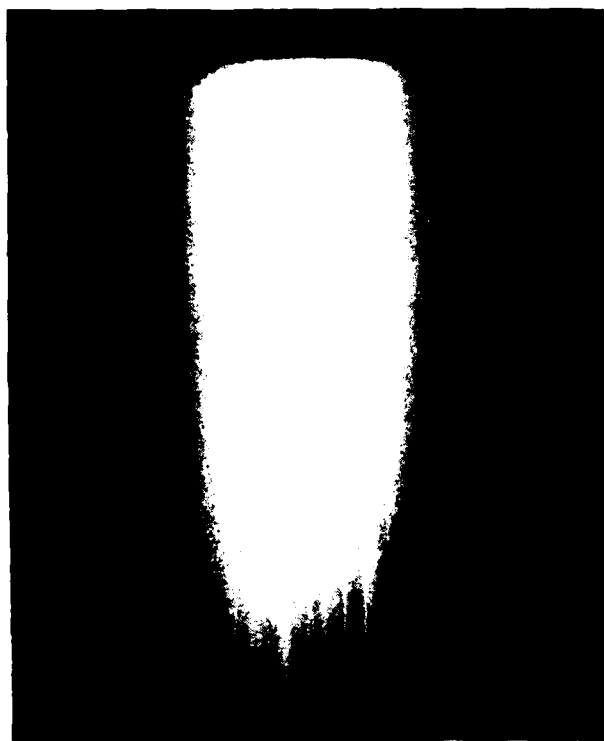


Fig. 10. a) 1,5-hexadiene (85-030)

b) 1,5-hexadiene (85-041)

c) 2,4-hexadiene (85-031)



Fig. 11. 2-butyne (85-027)

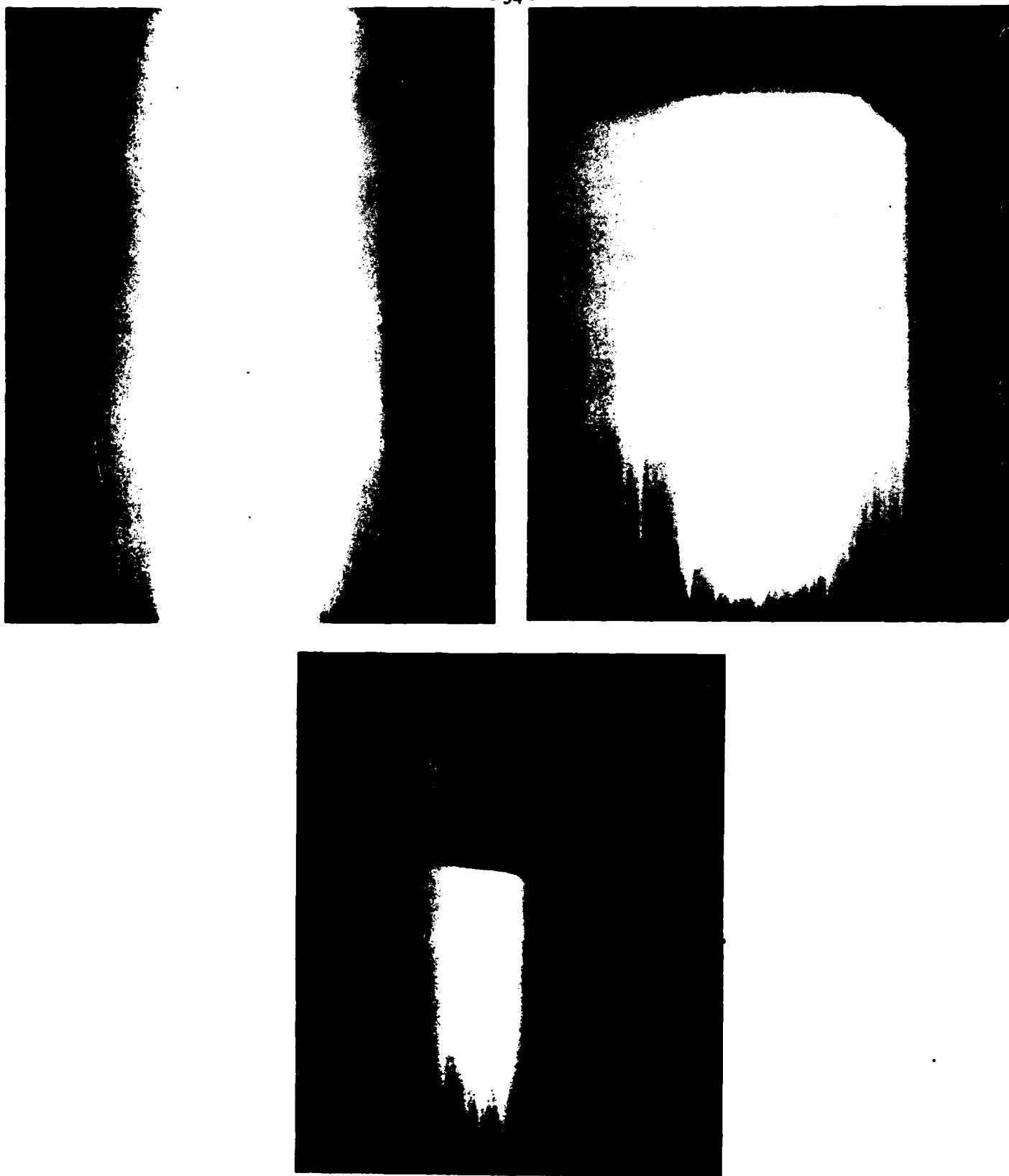


Fig. 12. a) benzene (84-053)

b) benzene (84-052)

c) nitro benzene (85-003)

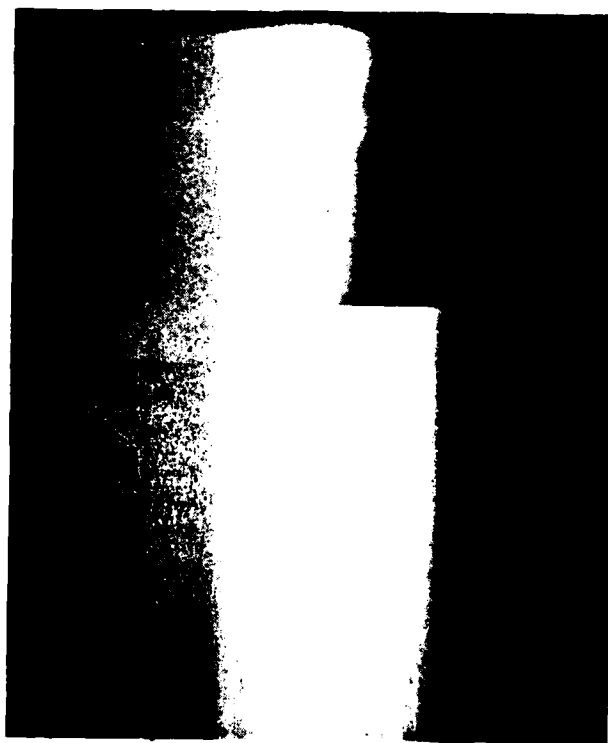
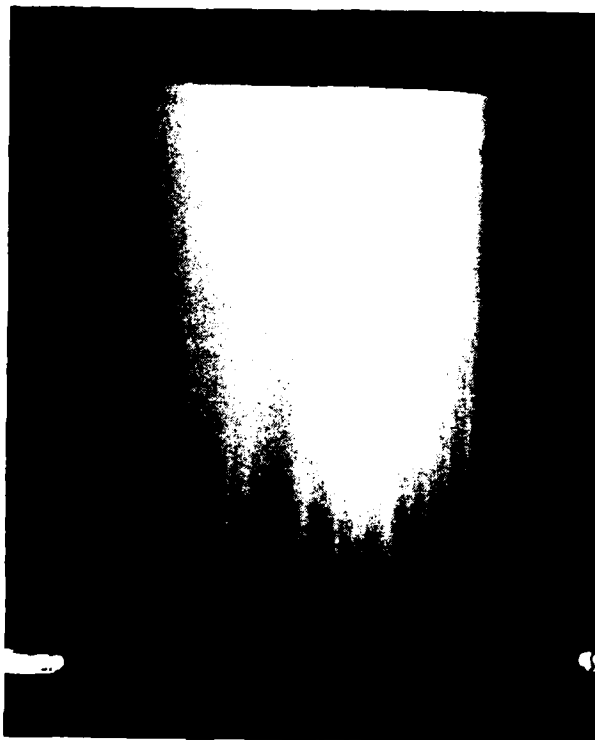
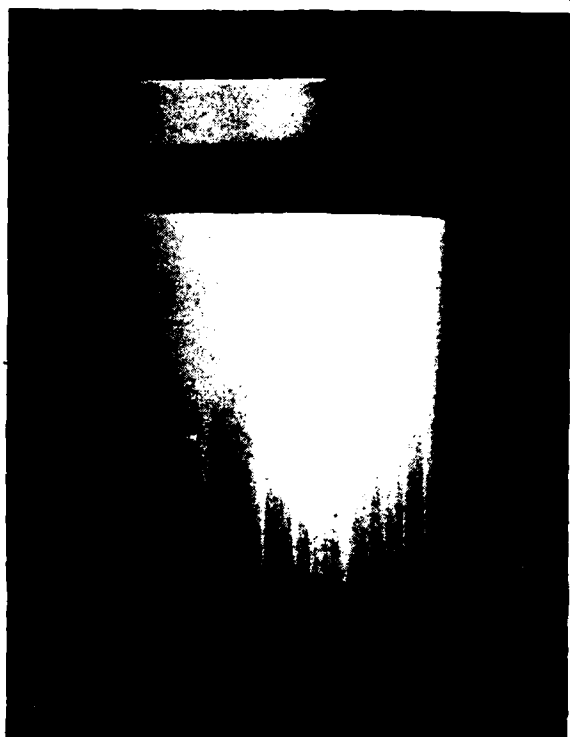


Fig. 13. a) carbon disulfide (84-049)

b) carbon disulfide (84-051)

c) 5 vol % CS_2 in Hexane (84-050)

d) CS_2 thin cell (85-034)

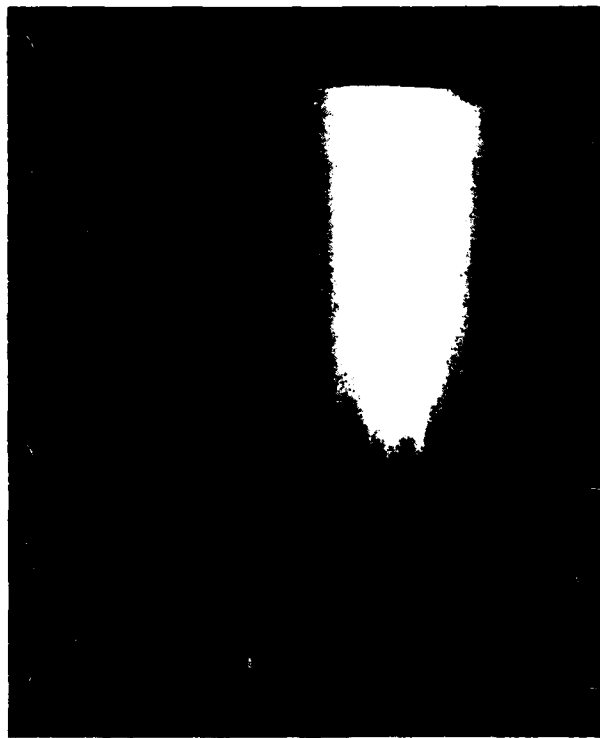
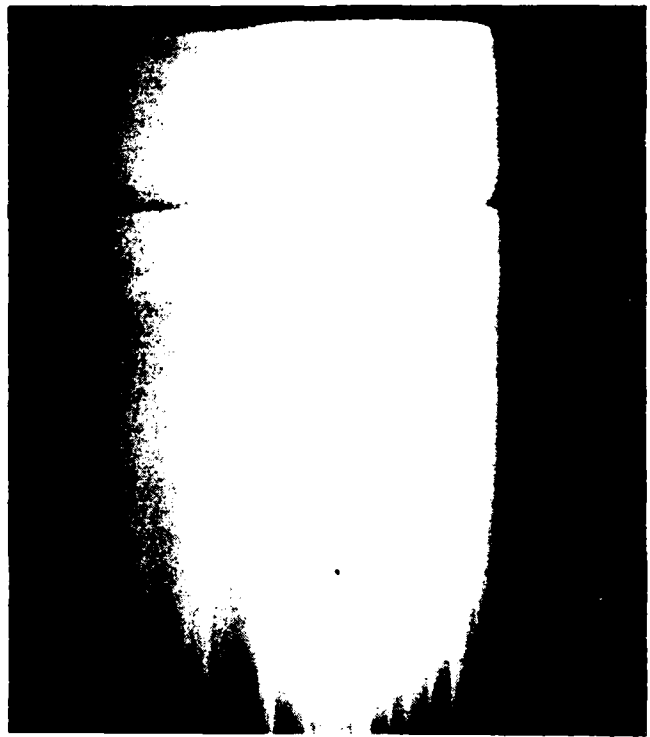
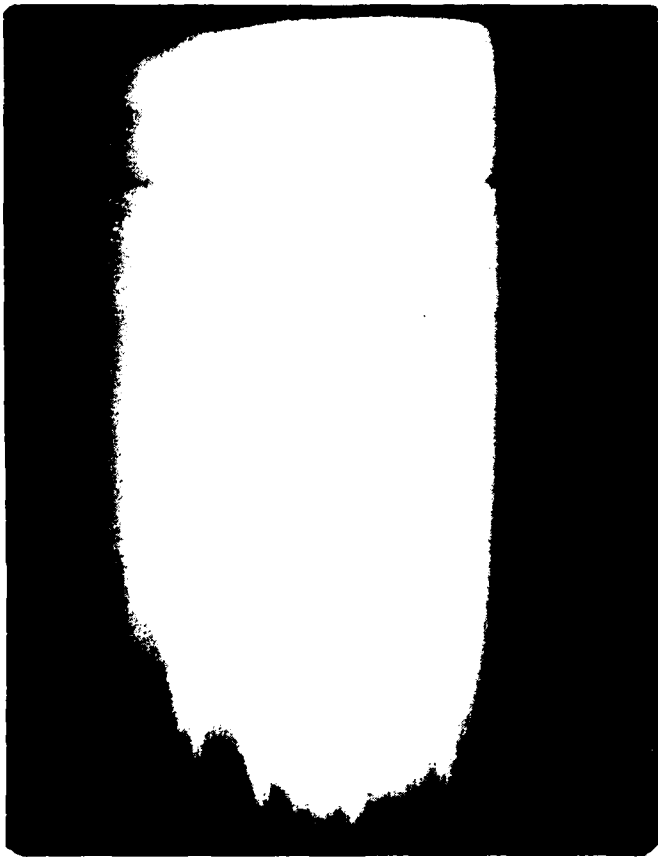


Fig. 14. a) water (84-040)

b) water (84-048)

c) hydrogen iodide (85-033)

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